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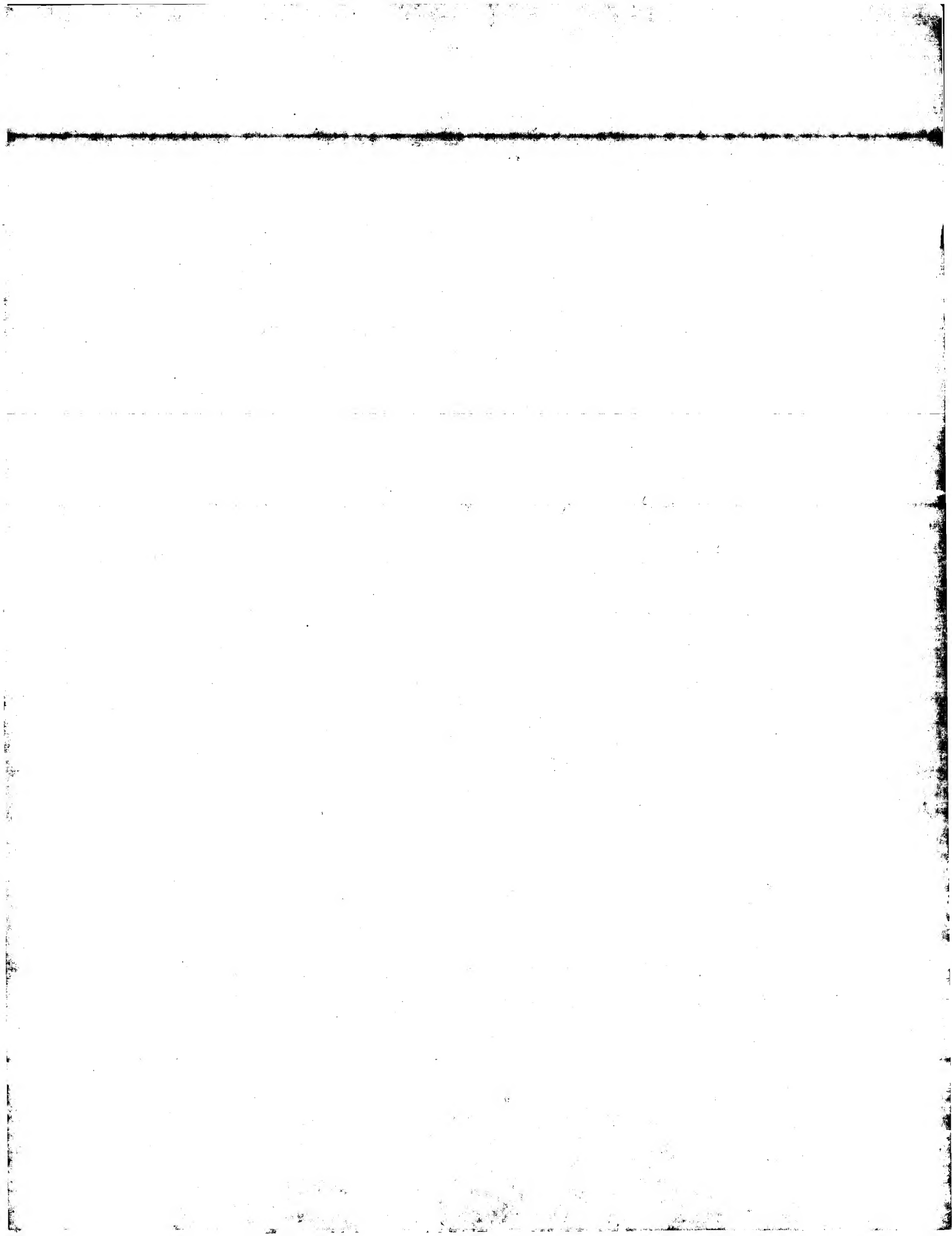
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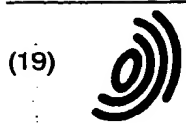
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(71) Applicant:
**THE GOODYEAR TIRE & RUBBER COMPANY
Akron, Ohio 44316-0001 (US)**

(72) Inventors:
• **Blok, Edward John
Wadsworth, Ohio 44281 (US)**
• **Sandstrom, Paul Harry
Tallmadge, Ohio 44278 (US)**

- **Losey, Cheryl Ann
Kent, Ohio 44240 (US)**
- **Halasa, Adel Farhan
Bath, Ohio 44333 (US)**
- **Hsu, Wen-Liang
Cuyahoga Falls, Ohio 44223 (US)**
- **Zanzig, David John
Uniontown, Ohio 44685 (US)**
- **Verthe, John Joseph Andre
Kent, Ohio 44240 (US)**

(74) Representative: **Leltz, Paul
Goodyear Technical Center-Luxembourg
Patent-Department
L-7750 Colmar-Berg (LU)**

(54) **Tire tread compound**

(57) This invention relates to a tire tread compound that is easily processable which can be used to improve the treadwear, rolling resistance and traction characteristics of tires. The tire tread compounds of this invention are a blend of tin-coupled polybutadiene, high vinyl polybutadiene and natural rubber. This blend of low glass transition temperature rubber and high glass transition temperature rubber is surprisingly easy to process which makes the concept of this invention commercially feasible. Thus, the tire tread compounds of this invention can be utilized in making tires having greatly improved traction characteristics and treadwear without sacrificing rolling resistance. These improved properties may be due, in part, to better interaction and compatibility with carbon black and/or silica fillers. The polybutadiene in the blend can be asymmetrical tin-coupled to further improve the cold flow characteristics of the rubber blend. Asymmetrical tin coupling in general also leads to better processability and other beneficial properties. This invention more specifically discloses a tire tread rubber composition which is comprised of (1) from 20 phr to 60 phr of tin-coupled polybutadiene rubber, (2) from 20 phr to 60 phr of a rubber selected from the group consisting of natural rubber and synthetic polyisoprene and (3) from 5 phr to 40 phr of high vinyl polybutadiene rubber.

Description

Background of the Invention

5 [0001] It is highly desirable for tires to exhibit good traction characteristics on both dry and wet surfaces. However, it has traditionally been very difficult to improve the traction characteristics of a tire without compromising its rolling resistance and tread wear. Low rolling resistance is important because good fuel economy is virtually always an important consideration. Good tread wear is also an important consideration because it is generally the most important factor which determines the life of the tire.

10 [0002] The traction, tread wear and rolling resistance of a tire is dependent to a large extent on the dynamic viscoelastic properties of the elastomers utilized in making the tire tread. In order to reduce the rolling resistance of a tire, rubbers having a high rebound have traditionally been utilized in making the tire's tread. On the other hand, in order to increase the wet skid resistance of a tire, rubbers which undergo a large energy loss have generally been utilized in the tire's tread. In order to balance these two viscoelastically inconsistent properties, mixtures of various types of synthetic and natural rubber are normally utilized in tire treads. For instance, various mixtures of styrene-butadiene rubber and polybutadiene rubber are commonly used as a rubber material for automobile tire treads. However, such blends are not totally satisfactory for all purposes.

15 [0003] Rubbers having intermediate glass transition temperatures (-70°C to -40°C) compromise rolling resistance and treadwear without significantly increasing traction characteristics. For this reason, blends of rubbers having low glass transition temperatures and rubbers having high glass transition temperatures are frequently utilized to attain improved traction characteristics without significantly compromising rolling resistance or treadwear. However, such blends of rubbers having low glass transition temperatures and rubbers having high glass transition temperatures exhibit poor processability. This major disadvantage associated with such blends has greatly hampered their utilization in making tire tread compounds.

20 [0004] Tin-coupled polymers are known to provide desirable properties, such as improved treadwear and reduced rolling resistance, when used in tire tread rubbers. Such tin-coupled rubbery polymers are typically made by coupling the rubbery polymer with a tin coupling agent at or near the end of the polymerization used in synthesizing the rubbery polymer. In the coupling process, live polymer chain ends react with the tin coupling agent thereby coupling the polymer. For instance, up to four live chain ends can react with tin tetrahalides, such as tin tetrachloride, thereby coupling the polymer chains together.

Summary of the Invention

25 [0005] This invention relates to a tire tread compound that is easily processable which can be used to improve the treadwear, rolling resistance and traction characteristics of tires. The tire tread compounds of this invention are a blend of tin-coupled polybutadiene, high vinyl polybutadiene and natural rubber. This blend of low glass transition temperature rubber and high glass transition temperature rubber is surprisingly easy to process which makes the concept of this invention commercially feasible. Thus, the tire tread compounds of this invention can be utilized in making tires having greatly improved traction characteristics and treadwear without sacrificing rolling resistance. These improved properties may be due, in part, to better interaction and compatibility with carbon black and/or silica fillers. The polybutadiene in the blend can be asymmetrically tin-coupled to further improve the cold flow characteristics of the rubber blend. Asymmetrical tin coupling in general also leads to better processability and other beneficial properties.

30 [0006] This invention more specifically discloses a tire tread rubber composition which is comprised of (1) from 20 phr to 60 phr of tin-coupled polybutadiene rubber, (2) from 20 phr to 60 phr of a rubber selected from the group consisting of natural rubber and synthetic polyisoprene and (3) from 5 phr to 40 phr of high vinyl polybutadiene rubber.

35 [0007] It is normally preferred for the tin-coupled polybutadiene rubber to be asymmetrically tin-coupled. In such cases, the stability of blends containing asymmetrical tin-coupled polybutadiene rubber can be improved by adding a tertiary chelating amine thereto subsequent to the time at which the tin-coupled rubbery polymer is coupled. N,N,N',N'-tetramethylethylenediamine (TMEDA) is a representative example of a tertiary chelating amine which is preferred for utilization in stabilizing the polymer blends of this invention.

Detailed Description of the Invention

40 [0008] The tire tread rubber compositions of this invention are comprised of (1) from 20 phr to 60 phr of tin-coupled polybutadiene rubber, (2) from 20 phr to 60 phr of a rubber selected from the group consisting of natural rubber and synthetic polyisoprene and (3) from 5 phr to 40 phr of high vinyl polybutadiene rubber. These tire tread rubbers will typically contain from 25 phr to 55 phr of the tin-coupled polybutadiene rubber, from 25 phr to 55 phr of the rubber selected from the group consisting of natural rubber and synthetic polyisoprene and from 10 phr to 30 phr of the high vinyl polyb-

utadiene rubber. It is normally preferred for the tire tread rubber to contain from 30 phr to 50 phr of the tin-coupled polybutadiene rubber, from 30 phr to 50 phr of the rubber selected from the group consisting of natural rubber and synthetic polyisoprene and from 15 phr to 25 phr of the high vinyl polybutadiene rubber.

[0009] The high vinyl polybutadiene rubber employed in the blends of this invention will normally have a glass transition temperature which is within the range of -40°C to $+40^{\circ}\text{C}$ and a Mooney ML 1+4 viscosity which is within the range of 30 to 100. The high vinyl polybutadiene rubber employed in the blends of this invention will preferably have a glass transition temperature which is within the range of -35°C to 0°C and a Mooney ML 1+4 viscosity which is within the range of 40 to 90. The high vinyl polybutadiene rubber employed in the blends of this invention will preferably have a glass transition temperature which is within the range of -30°C to -20°C and a Mooney ML 1+4 viscosity which is within the range of 60 to 80.

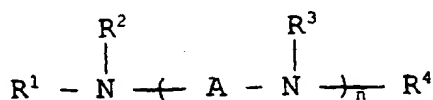
[0010] The tin-coupled polybutadiene will typically have a Mooney ML 1+4 viscosity which is within the range of 5 to 40 before coupling and a Mooney ML 1+4 viscosity of 60 to 120 after coupling. The tin-coupled polybutadiene will preferably have a Mooney ML 1+4 viscosity which is within the range of 5 to 35 before coupling and a Mooney ML 1+4 viscosity of 75 to 110 after coupling. The tin-coupled polybutadiene will most preferably have a Mooney ML 1+4 viscosity which is within the range of 10 to 30 before coupling and a Mooney ML 1+4 viscosity of 80 to 100 after coupling.

[0011] The tin-coupled polybutadiene will typically be prepared by reacting "living" polybutadiene having lithium end groups with a tin halide, such as tin tetrachloride. This coupling step will normally be carried out as a batch process. However, it is generally preferred to tin-couple the polybutadiene in a continuous process which results in the formation of asymmetrically tin-coupled polybutadiene rubber.

[0012] The tin coupling agent employed in making asymmetrically tin-coupled polybutadiene rubber will normally be a tin tetrahalide, such as tin tetrachloride, tin tetrabromide, tin tetrafluoride or tin tetraiodide. However, tin trihalides can also optionally be used. In cases where tin trihalides are utilized, a coupled polymer having a maximum of three arms results. To induce a higher level of branching, tin tetrahalides are normally preferred. As a general rule, tin tetrachloride is most preferred.

[0013] Broadly, and exemplary, a range of 0.01 to 4.5 milliequivalents of tin coupling agent is employed per 100 grams of the rubbery polymer. It is normally preferred to utilize 0.01 to 1.5 milliequivalents of the tin coupling agent per 100 grams of polymer to obtain the desired Mooney viscosity. The larger quantities tend to result in production of polymers containing terminally reactive groups or insufficient coupling. One equivalent of tin coupling agent per equivalent of lithium is considered an optimum amount for maximum branching. For instance, if a tin tetrahalide is used as the coupling agent, one mole of the tin tetrahalide would be utilized per four moles of live lithium ends. In cases where a tin trihalide is used as the coupling agent, one mole of the tin trihalide will optimally be utilized for every three moles of live lithium ends. The tin coupling agent can be added in a hydrocarbon solution, e.g., in cyclohexane, to the polymerization admixture in the reactor with suitable mixing for distribution and reaction.

[0014] After the tin coupling has been completed, a tertiary chelating alkyl 1,2-ethylene diamine can optionally be added to the polymer cement to stabilize the tin-coupled rubbery polymer. This technique for stabilization of the tin-coupled rubber is more fully described in US-A-5 739 182. The tertiary chelating amines which can be used for stabilization are normally chelating alkyl diamines of the structural formula:



wherein n represents an integer from 1 to 6, wherein A represents an alkane group containing from 1 to 6 carbon atoms and wherein R^1 , R^2 , R^3 and R^4 can be the same or different and represent alkane groups containing from 1 to 6 carbon atoms. The alkane group A is the formula $\{\text{CH}_2\}_m$ wherein m is an integer from 1 to 6. The alkane group will typically contain from 1 to 4 carbon atoms (m will be 1 to 4) and will preferably contain 2 carbon atoms. In most cases, n will be an integer from 1 to 3 with it being preferred for n to be 1. It is preferred for R^1 , R^2 , R^3 and R^4 to represent alkane groups which contain from 1 to 3 carbon atoms. In most cases, R^1 , R^2 , R^3 and R^4 will represent methyl groups.

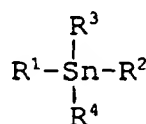
[0015] A sufficient amount of the chelating amine should be added to complex with any residual tin coupling agent remaining after completion of the coupling reaction. In most cases, from 0.01 phr (parts by weight per 100 parts by weight of dry rubber) to 2 phr of the chelating alkyl 1,2-ethylene diamine will be added to the polymer cement to stabilize the rubbery polymer. Typically, from 0.05 phr to 1 phr of the chelating alkyl 1,2-ethylene diamine will be added. More typically, from 0.1 phr to 0.6 phr of the chelating alkyl 1,2-ethylene diamine will be added to the polymer cement to stabilize the rubbery polymer.

[0016] After the polymerization, asymmetrical tin coupling and optionally the stabilization step, has been completed, the tin-coupled rubbery polymer can be recovered from the organic solvent utilized in the solution polymerization. The

tin-coupled rubbery polymer can be recovered from the organic solvent and residue by means such as decantation, filtration, centrifugation and the like. It is often desirable to precipitate the tin-coupled rubbery polymer from the organic solvent by the addition of lower alcohols containing from 1 to 4 carbon atoms to the polymer solution. Suitable lower alcohols for precipitation of the rubber from the polymer cement include methanol, ethanol, isopropyl alcohol, normal-propyl alcohol and t-butyl alcohol. The utilization of lower alcohols to precipitate the tin-coupled rubbery polymer from the polymer cement also "kills" any remaining living polymer by inactivating lithium end groups. After the tin-coupled rubbery polymer is recovered from the solution, steam-stripping can be employed to reduce the level of volatile organic compounds in the tin-coupled rubbery polymer.

[0017] The asymmetrical tin-coupled polybutadiene rubber that can be employed in the blends of this invention are comprised of a tin atom having at least three polybutadiene arms covalently bonded thereto. At least one of the polybutadiene arms bonded to the tin atom has a number average molecular weight of less than 40,000 and at least one of the polybutadiene arms bonded to the tin atom has a number average molecular weight of at least 80,000. The ratio of the weight average molecular weight to the number average molecular weight of the asymmetrical tin-coupled polybutadiene rubber will also normally be within the range of 2 to 2.5.

[0018] The asymmetrical tin-coupled polybutadiene rubber that can be utilized in the blends of this invention is typically of the structural formula:



wherein R^1 , R^2 , R^3 and R^4 can be the same or different and are selected from the group consisting of alkyl groups and polybutadiene arms (polybutadiene rubber chains), with the proviso that at least three members selected from the group consisting of R^1 , R^2 , R^3 and R^4 are polybutadiene arms, with the proviso that at least one member selected from the group consisting of R^1 , R^2 , R^3 and R^4 is a low molecular weight polybutadiene arm having a number average molecular weight of less than 40,000, with the proviso that at least one member selected from the group consisting of R^1 , R^2 , R^3 and R^4 is a high molecular weight polybutadiene arm having a number average molecular weight of greater than 80,000, and with the proviso that the ratio of the weight average molecular weight to the number average molecular weight of the asymmetrical tin-coupled polybutadiene rubber is within the range of 2 to 2.5. It should be noted that R^1 , R^2 , R^3 and R^4 can be alkyl groups because it is possible for the tin halide coupling agent to react directly with alkyl lithium compounds which are used as the polymerization initiator.

[0019] In most cases, four polybutadiene arms will be covalently bonded to the tin atom in the asymmetrical tin-coupled polybutadiene rubber. In such cases, R^1 , R^2 , R^3 and R^4 will all be polybutadiene arms. The asymmetrical tin-coupled polybutadiene rubber will often contain a polybutadiene arm of intermediate molecular weight as well as the low molecular weight arm and the high molecular weight arm. Such intermediate molecular weight arms will have a molecular weight which is within the range of 45,000 to 75,000. It is normally preferred for the low molecular polybutadiene arm to have a molecular weight of less than 30,000, with it being most preferred for the low molecular weight arm to have a molecular weight of less than 25,000. It is normally preferred for the high molecular polybutadiene arm to have a molecular weight of greater than 90,000, with it being most preferred for the high molecular weight arm to have a molecular weight of greater than 100,000.

[0020] The tire tread rubber compositions of this invention can be compounded utilizing conventional ingredients and standard techniques. For instance, these tire tread rubber blends will typically be mixed with carbon black and/or silica, sulfur, fillers, accelerators, oils, waxes, scorch inhibiting agents and processing aids. In most cases, the rubber blend will be compounded with sulfur and/or a sulfur-containing compound, at least one filler, at least one accelerator, at least one antidegradant, at least one processing oil, zinc oxide, optionally a tackifier resin, optionally a reinforcing resin, optionally one or more fatty acids, optionally a peptizer and optionally one or more scorch inhibiting agents. Such blends will normally contain from 0.5 to 5 phr (parts per hundred parts of rubber by weight) of sulfur and/or a sulfur-containing compound with 1 phr to 2.5 phr being preferred. It may be desirable to utilize insoluble sulfur in cases where bloom is a problem.

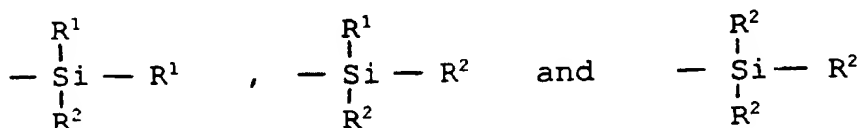
[0021] At least some silica will be utilized in the blend as a filler. The filler can, of course, be comprised totally of silica. However, in some cases, it will be beneficial to utilize a combination of silica and carbon black as the filler. Clays and/or talc can be included in the filler to reduce cost. The blend will also normally include from 0.1 to 2.5 phr of at least one accelerator with 0.2 to 1.5 phr being preferred. Antidegradants, such as antioxidants and antiozonants, will generally be included in the tread compound blend in amounts ranging from 0.25 to 10 phr with amounts in the range of 1 to 5 phr being preferred. Processing oils will generally be included in the blend in amounts ranging from 2 to 100 phr with

amounts ranging from 5 to 50 phr being preferred. The polybutadiene blends of this invention will also normally contain from 0.5 to 10 phr of zinc oxide with 1 to 5 phr being preferred. These blends can optionally contain from 0 to 10 phr of tackifier resins, 0 to 10 phr of reinforcing resins, 1 to 10 phr of fatty acids, 0 to 2.5 phr of peptizers and 0 to 1 phr of scorch inhibiting agents.

[0022] To fully realize the total advantages of the blends of this invention, silica will normally be included in the tread rubber formulation. The processing of the rubber blend is normally conducted in the presence of a sulfur containing organosilicon compound to realize maximum benefits. Examples of suitable sulfur-containing organosilicon compounds are of the formula:



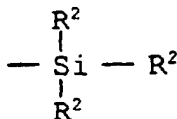
in which Z is selected from the group consisting of



where R¹ is an alkyl group of 1 to 4 carbon atoms, cyclohexyl or phenyl; wherein R² is alkoxy of 1 to 8 carbon atoms or cycloalkoxy of 5 to 8 carbon atoms; and wherein Alk is a divalent hydrocarbon of 1 to 18 carbon atoms and n is an integer of 2 to 8.

[0023] Specific examples of sulfur-containing organosilicon compounds which may be used in accordance with the present invention include: 3,3'-bis(trimethoxysilylpropyl) disulfide, 3,3'-bis(triethoxysilylpropyl) tetrasulfide, 3,3'-bis(triethoxysilylpropyl) octasulfide, 3,3'-bis(trimethoxysilylpropyl) tetrasulfide, 2,2'-bis(triethoxysilylethyl) tetrasulfide, 3,3'-bis(trimethoxysilylpropyl) trisulfide, 3,3'-bis(triethoxysilylpropyl) trisulfide, 3,3'-bis(tributoxysilylpropyl) disulfide, 3,3'-bis(trimethoxysilylpropyl) hexasulfide, 3,3'-bis(trimethoxysilylpropyl) octasulfide, 3,3'-bis(trioctoxysilylpropyl) tetrasulfide, 3,3'-bis(trihexoxysilylpropyl) disulfide, 3,3'-bis(tri-2"-ethylhexoxysilylpropyl) trisulfide, 3,3'-bis(triisooctoxysilylpropyl) tetrasulfide, 3,3'-bis(tri-t-butoxysilylpropyl) disulfide, 2,2'-bis(methoxy diethoxy silyl ethyl) tetrasulfide, 2,2'-bis(tripropoxysilylethyl) pentasulfide, 3,3'-bis(tricyclonoxoxysilylpropyl) tetrasulfide, 3,3'-bis(tricyclopentoxysilylpropyl) trisulfide, 2,2'-bis(tri-2"-methylcyclohexoxysilylethyl) tetrasulfide, bis(trimethoxysilylmethyl) tetrasulfide, 3-methoxy ethoxy propoxysilyl 3'-diethoxybutoxysilylpropyltetrasulfide, 2,2'-bis(dimethyl methoxysilylethyl) disulfide, 2,2'-bis(dimethyl sec.butoxysilylethyl) trisulfide, 3,3'-bis(methyl butylethoxysilylpropyl) tetrasulfide, 3,3'-bis(di t-butylmethoxysilylpropyl) tetrasulfide, 2,2'-bis(phenyl methyl methoxysilylethyl) trisulfide, 3,3'-bis(diphenyl isopropoxysilylpropyl) tetrasulfide, 3,3'-bis(diphenyl cyclohexoxysilylpropyl) disulfide, 3,3'-bis(dimethyl ethylmercaptosilylpropyl) tetrasulfide, 2,2'-bis(methyl dimethoxysilylethyl) trisulfide, 2,2'-bis(methyl ethoxypropoxysilylethyl) tetrasulfide, 3,3'-bis(diethyl methoxysilylpropyl) tetrasulfide, 3,3'-bis(ethyl di-sec. butoxysilylpropyl) disulfide, 3,3'-bis(propyl diethoxysilylpropyl) disulfide, 3,3'-bis(butyl dimethoxysilylpropyl) trisulfide, 3,3'-bis(phenyl dimethoxysilylpropyl) tetrasulfide, 3-phenyl ethoxybutoxysilyl 3'-trimethoxysilylpropyl tetrasulfide, 4,4'-bis(trimethoxysilylbutyl) tetrasulfide, 6,6'-bis(triethoxysilylhexyl) tetrasulfide, 12,12'-bis(triisopropoxysilyl dodecyl) disulfide, 18,18'-bis(trimethoxysilyloctadecyl) tetrasulfide, 18,18'-bis(tripropoxysilyloctadecenyl) tetrasulfide, 4,4'-bis(trimethoxysilyl-buten-2-yl) tetrasulfide, 4,4'-bis(trimethoxysilylcyclohexylene) tetrasulfide, 5,5'-bis(dimethoxymethylsilylpentyl) trisulfide, 3,3'-bis(trimethoxysilyl-2-methylpropyl) tetrasulfide, 3,3'-bis(dimethoxyphenylsilyl-2-methylpropyl) disulfide.

[0024] The preferred sulfur-containing organosilicon compounds are the 3,3'-bis(trimethoxy or triethoxy silylpropyl) disulfides. The most preferred compound is 3,3'-bis(triethoxysilylpropyl) tetrasulfide. Therefore, as to Formula I, preferably Z is



where R² is an alkoxy of 2 to 4 carbon atoms, with 2 carbon atoms being particularly preferred; Alk is a divalent hydrocarbon of 2 to 4 carbon atoms with 3 carbon atoms being particularly preferred; and n is an integer of from 3 to 5 with 4 being particularly preferred.

[0025] The amount of the sulfur-containing organosilicon compound of Formula I in a rubber composition will vary, depending on the level of silica that is used. Generally speaking, the amount of the compound of Formula I will range from 0.01 to 1.0 parts by weight per part by weight of the silica. Preferably, the amount will range from 0.02 to 0.4 parts by weight per part by weight of the silica. More preferably, the amount of the compound of formula I will range from 0.05 to 0.25 parts by weight per part by weight of the silica.

[0026] In addition to the sulfur-containing organosilicon, the rubber composition should contain a sufficient amount of silica, and carbon black, if used, to contribute a reasonably high modulus and high resistance to tear. The silica filler may be added in amounts ranging from 10 phr to 250 phr. Preferably, the silica is present in an amount ranging from 15 phr to 80 phr. If carbon black is also present, the amount of carbon black, if used, may vary. Generally speaking, the amount of carbon black will vary from 5 phr to 80 phr. Preferably, the amount of carbon black will range from 10 phr to 40 phr. It is to be appreciated that the silica coupler may be used in conjunction with a carbon black, namely pre-mixed with a carbon black prior to addition to the rubber composition, and such carbon black is to be included in the aforesaid amount of carbon black for the rubber composition formulation. In any case, the total quantity of silica and carbon black will be at least 30 phr. The combined weight of the silica and carbon black, as hereinbefore referenced, may be as low as about 30 phr, but is preferably from 45 to 130 phr.

[0027] The commonly employed siliceous pigments used in rubber compounding applications can be used as the silica in this invention, including pyrogenic and precipitated siliceous pigments (silica), although precipitate silicas are preferred. The siliceous pigments preferably employed in this invention are precipitated silicas such as, for example, those obtained by the acidification of a soluble silicate; e.g., sodium silicate.

[0028] Such silicas might be characterized, for example, by having a BET surface area, as measured using nitrogen gas, preferably in the range of 40 to 600, and more usually in a range of 50 to 300 square meters per gram. The BET method of measuring surface area is described in the *Journal of the American Chemical Society*, Volume 60, page 304 (1930).

[0029] The silica may also be typically characterized by having a dibutylphthalate (DBP) absorption value in a range of 100 to 400, and more usually 150 to 300. The silica might be expected to have an average ultimate particle size, for example, in the range of 0.01 to 0.05 micron as determined by the electron microscope, although the silica particles may be even smaller, or possibly larger, in size.

[0030] Various commercially available silicas may be considered for use in this invention such as, only for example herein, and without limitation, silicas commercially available from PPG Industries under the Hi-Sil trademark with designations 210, 243, etc; silicas available from Rhone-Poulenc, with, for example, designations of Z1165MP and Z165GR and silicas available from Degussa A.G. with, for example, designations VN2 and VN3.

[0031] Tire tread formulations which include silica and an organosilicon compound will typically be mixed utilizing a thermomechanical mixing technique. The mixing of the tire tread rubber formulation can be accomplished by methods known to those having skill in the rubber mixing art. For example, the ingredients are typically mixed in at least two stages, namely at least one non-productive stage followed by a productive mix stage. The final curatives including sulfur-vulcanizing agents are typically mixed in the final stage which is conventionally called the "productive" mix stage in which the mixing typically occurs at a temperature, or ultimate temperature, lower than the mix temperature(s) than the preceding non-productive mix stage(s). The rubber, silica and sulfur-containing organosilicon, and carbon black, if used, are mixed in one or more non-productive mix stages. The terms "non-productive" and "productive" mix stages are well known to those having skill in the rubber mixing art. The sulfur-vulcanizable rubber composition containing the sulfur-containing organosilicon compound, vulcanizable rubber and generally at least part of the silica should be subjected to a thermomechanical mixing step. The thermomechanical mixing step generally comprises a mechanical working in a mixer or extruder for a period of time suitable in order to produce a rubber temperature between 140°C and 190°C. The appropriate duration of the thermomechanical working varies as a function of the operating conditions and the volume and nature of the components. For example, the thermomechanical working may be for a duration of time which is within the range of 2 minutes to 20 minutes. It will normally be preferred for the rubber to reach a temperature which is within the range of 145°C to 180°C and to be maintained at said temperature for a period of time which is within the range of 4 minutes to 12 minutes. It will normally be more preferred for the rubber to reach a temperature which is within the range of 155°C to 170°C and to be maintained at said temperature for a period of time which is within the range of 5 minutes to 10 minutes.

[0032] The tire tread compounds of this invention can be used in tire treads in conjunction with ordinary tire manufacturing techniques. Tires are built utilizing standard procedures with the polybutadiene rubber blend simply being substituted for the rubber compounds typically used as the tread rubber. After the tire has been built with the polybutadiene rubber-containing blend, it can be vulcanized using a normal tire cure cycle. Tires made in accordance with this invention can be cured over a wide temperature range. However, it is generally preferred for the tires of this invention to be cured at a temperature ranging from 132°C (270°F) to 166°C (330°F). It is more typical for the tires of this invention to be cured at a temperature ranging from 143°C (290°F) to 154°C (310°F). It is generally preferred for the cure cycle used to vulcanize the tires of this invention to have a duration of 10 to 20 minutes with a cure cycle of 12 to 18 minutes being

most preferred.

[0033] By utilizing the rubber blends of this invention in tire tread compounds, traction characteristics can be improved without compromising tread wear or rolling resistance. Since the polybutadiene rubber blends of this invention do not contain styrene, the cost of raw materials can also be reduced. This is because styrene and other vinyl aromatic monomers are expensive relative to the cost of 1,3-butadiene.

[0034] This invention is illustrated by the following examples which are merely for the purpose of illustration and are not to be regarded as limiting the scope of the invention or the manner in which it can be practiced. Unless specifically indicated otherwise, parts and percentages are given by weight.

Example 1

[0035] In this experiment, a tin-coupled polybutadiene rubber was prepared in a 10-gallon (38 liter) batch reactor at a temperature of 70°C. In the procedure used, 22,400 grams of a silica/molecular sieve/aluminum dried premix containing 17.5 weight percent of 1,3-butadiene in hexanes was charged into the 10-gallon reactor. After the amount of impurity in the premix was determined, 28.8 ml of 1.6 M solution of n-butyl lithium (in hexane) was added to the reactor. The target Mn (number averaged molecular weight) was 100,000. The polymerization was allowed to proceed at 70°C for two hours. An analysis of the residual monomer indicated that all monomers were totally consumed. After a small aliquot of polymer cement was removed from the reactor (for analysis), 9.2 ml of a 0.65 M solution of tin tetrachloride (in hexane) was added to the reactor and the coupling reaction was carried out at the same temperature for 30 minutes. At this time, 1.5 phr (parts per 100 parts by weight of rubber) of antioxidant was added to the reactor to shortstop the polymerization and to stabilize the polymer.

[0036] After the hexane solvent was evaporated, the resulting tin-coupled polybutadiene was dried in a vacuum oven at 50°C. The tin-coupled polybutadiene was determined to have a glass transition temperature (T_g) at -95°C. It was also determined to have a microstructure which contained 8 percent 1,2-polybutadiene units and 92 percent 1,4-polybutadiene units. The Mooney viscosity (ML 1+4 @ 100°C) of the tin-coupled polybutadiene made was determined to be 110. The Mooney Viscosity of the base polybutadiene rubber was also determined to be 11.

Example 2

[0037] In this experiment, asymmetrically tin-coupled polybutadiene was synthesized in a three-reactor (2 gallons each) continuous system at 90°C. A premix containing 15 percent 1,3-butadiene in hexane was charged into the first reactor continuously at a rate of 117 grams/minute. Polymerization was initiated by adding a 0.128 M solution of n-butyl lithium into the first reactor at a rate of 0.82 grams/minute. Most of monomers were exhausted at the end of second reactor and the polymerization medium containing live lithium ends was continuously pushed into the third reactor where the coupling agent, tin tetrachloride (0.025 M solution in hexane), was added at a rate of 1.16 grams/minutes. The residence time for all three reactors was set at 1.5 hours to achieve complete monomer conversion in the second reactor and complete coupling in the third reactor. The polymerization medium was then continuously pushed over to a holding tank containing a shortstop and an antioxidant. The resulting polymer cement was then steam-stripped and the asymmetrical tin-coupled polybutadiene recovered was dried in an oven at 60°C. The polymer was determined to have a glass transition temperature at -95°C and have a Mooney ML 1+4 @ 100°C viscosity of 94. It was also determined to have a microstructure which contained 8 percent 1,2-polybutadiene units and 92 percent 1,4-polybutadiene units. The precursor of this polymer (i.e., base polymer prior to coupling) was also determined to have an ML 1+4 @ 100°C of 20.

Examples 3-4 and Comparative Examples 5-8

[0038] In this series of experiments, various rubber blends were prepared and evaluated as tire tread rubber compositions. These blends were prepared by a three-step mixing process. In the first step, non-productive blends were made by mixing the rubbers shown in Table I with 7.0 parts of processing aids, 3 parts of zinc oxide, 2 parts of stearic acid and 0.15 parts of 2,2'-dibenzamidodiphenyl disulfide. This first non-productive mixing step was carried out over a period of about 4 minutes which resulted in a temperature of about 160°C being attained.

[0039] In the procedure used, 12 parts of fine particle-size hydrated silica, 2.25 parts of a 50 percent/50 percent blend of silica and carbon black (X50S from Degussa A.G.) and 3 parts of a naphthenic/paraffinic process oil were added to the blend in a second non-productive mixing step. This second non-productive mixing step was carried out over a period of about 3 minutes to a temperature of about 150°C.

[0040] A productive compound was then made by mixing 0.66 parts of diaryl-p-phenylenediamine, 1.12 parts of N-tert-butyl-2-benzothiazole, 0.14 parts of tetramethylthiuram disulfide and 1.5 parts of rubber makers sulfur into the blend. This productive mixing step was carried out over a period of about 2.5 minutes to a drop temperature of about 120°C. Then, the tire tread rubber compounds were cured and evaluated. The results of this evaluation are shown in

Table I.

TABLE I

Example	3	4	5
Natural Rubber ¹	40	49	40
Isoprene-Butadiene Rubber ²		45	
3,4-Polyisoprene ³		6	
High Vinyl Polybutadiene ⁴	20		20
Polybutadiene Rubber ⁵	40		
Tin-Coupled Polybutadiene ⁶			40
Carbon Black ⁷	38		38
Silica ⁸	12		12
Rheometer 150°C			
Min torque	11	11	9.6
Max torque	40.8	41.3	42
delta torque	29.8	30.3	32.4
T25	6	6.25	6.75
T90	9.75	9.75	10.5
ATS 18@150			
100% Modulus, MPa	2.39	2.35	2.31
300% Modulus, MPa	11.07	11.09	11.83
Brk Str, MPa	16.61	19.27	16.94
EL-Brk, %	441	489	418
Hardness, RT	61.6	61.6	60.9
Hardness, 100°C	58.8	58.4	58.2
Rebound RT %	56.8	56.1	61
Rebound, 100°C	68.9	71.4	71.9
DIN	73	96	72
Tan Delta -40	0.53	0.43	0.51
-30	0.32	0.26	0.30
-20	0.22	0.18	0.20
-10	0.15	0.14	0.13
0	0.13	0.13	0.12

¹ TSR20² 30% Isoprene/70% Butadiene,T_g = -82°C, Mooney ML/4 @ 100°C = 85³ 365% 3,4-structure, Mooney ML/4 @ 100°C = 70⁴ 80% Vinyl; 82 Mooney, T_g2⁵ Budene 1209 from -28°C⁶ Polymer of Example 1⁷ ASTM N-299⁸ HiSil® 210 from PPG Industries

[0041] It is well known that Sn-coupled polymers provide improvements in processing over their linear counterparts.

You see an example of this when comparing the Rheometer minimum torque values of Example 5 versus Example 3. The compound of Example 5 contains tin-coupled polybutadiene and has the lower minimum torque. The rebound values of the compound containing the tin-coupled polybutadiene (Example 5) are higher than for the control Example 3, suggesting better rolling resistance (RR) for the compound containing the tin-coupled polybutadiene.

[0042] Example 4 is an example of current passenger tread technology. This tread contains a blend of three polymers: (1) NR for processing and traction, (2) IBR for processing, treadwear and RR and (3) 3,4 polyisoprene for traction. The compound of this invention (Example 5) also uses a blend of three polymers, including NR, high vinyl polybutadiene for traction and Sn-coupled polybutadiene for processing, RR and treadwear.

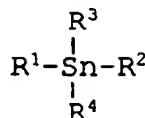
[0043] The lab data (Table I) clearly shows the superiority of the new polymer system over that of the current polymer system. The new polymer system provides improved treadwear (DIN abrasion resistance improved 25 percent), along with reduced rolling resistance (RT rebound values increased 9 percent). The wet traction (measured by the tan delta values from -40°C through 0°C) should be equal between the two compounds, as can be seen from the tan delta values reported in Table I. It should be noted that higher tan delta values in the range of -40°C to 0°C are predictive of better wet reaction characteristics in tires.

[0044] In summary, the new polymer system (Example 5) improves the tradeoff between RR, treadwear and wet traction versus current technology (Example 4) and the control polymer system (Example 3).

[0045] While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the scope of the appended claims.

Claims

1. A tire tread rubber composition which is characterized by being comprised of (1) from 20 phr to 60 phr of tin-coupled polybutadiene rubber, (2) from 20 phr to 60 phr of a rubber selected from the group consisting of natural rubber and synthetic polyisoprene and (3) from 5 phr to 40 phr of high vinyl polybutadiene rubber.
2. A tire tread rubber composition as specified in claim 1 characterized in that said tin-coupled polybutadiene rubber has a Mooney viscosity which is within the range of 60 to 120.
3. A tire tread rubber composition as specified in claim 2 characterized in that said tin-coupled polybutadiene rubber is tin-coupled in a batch process.
4. A tire tread rubber composition as specified in claim 2 characterized in that said tin-coupled polybutadiene rubber is tin-coupled in a continuous process.
5. A tire tread rubber composition as specified in claim 2 characterized in that said tin-coupled polybutadiene is asymmetrically tin-coupled polybutadiene.
6. A tire tread rubber composition as specified in claim 2 characterized in that said high vinyl polybutadiene rubber has a glass transition temperature which is within the range of -40°C to 40°C and a Mooney viscosity which is within the range of 30 to 100.
7. A tire tread rubber composition as specified in any of the preceding claims characterized in that the tire tread rubber composition contains from 25 phr to 55 phr of the tin-coupled polybutadiene rubber, from 25 phr to 55 phr of the rubber selected from the group consisting of natural rubber and synthetic polyisoprene and from 10 phr to 30 phr of the high vinyl polybutadiene rubber; in that the high vinyl polybutadiene rubber has a glass transition temperature which is within the range of -35°C to 0°C and a Mooney viscosity which is within the range of 40 to 90; and in that said tin-coupled polybutadiene rubber has a Mooney viscosity which is within the range of 75 to 110.
8. A tire tread rubber composition as specified in claim 5 characterized in that said asymmetrically tin-coupled polybutadiene is of the structural formula:



wherein R^1 , R^2 , R^3 and R^4 can be the same or different and are selected from the group consisting of alkyl groups and polybutadiene arms, with the proviso that at least three members selected from the group consisting of R^1 , R^2 , R^3 and R^4 are polybutadiene arms, with the proviso that at least one member selected from the group consisting of R^1 , R^2 , R^3 and R^4 is a low molecular weight polybutadiene arm having a number average molecular weight of less than 40,000, with the proviso that at least one member selected from the group consisting of R^1 , R^2 , R^3 and R^4 is a high molecular weight polybutadiene arm having a number average molecular weight of greater than 80,000 and with the proviso that the ratio of the weight average molecular weight to the number average molecular weight of the asymmetrical tin-coupled polybutadiene rubber is within the range of 2 to 2.5.

9. A tire tread rubber composition as specified in claim 8 characterized in that R^1 , R^2 , R^3 and R^4 are all polybutadiene arms; in that the low molecular weight polybutadiene arm has a molecular weight of less than 30,000; and in that the high molecular weight polybutadiene arm has a molecular weight of greater than 90,000.
10. A tire tread rubber composition as specified in any of the preceding claims characterized in that said composition is further comprised of 70 phr to 250 phr of silica; in that carbon black is present in said composition in an amount which is no greater than 10 phr; in that said composition is further comprised of a silica coupling agent; and in that the silica and the silica coupling agent are mixed into the composition utilizing a thermomechanical mixing technique wherein the rubber composition is maintained at a temperature which is within the range of 145°C to 180°C for 4 minutes to 12 minutes.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 98 11 7472

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 647 675 A (SUMITOMO RUBBER IND) 12 April 1995 * claim 2 *	1-10	C08L21/00 B60C1/00
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			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C08L B60C
The present search report has been drawn up for all claims			

Place of search

THE HAGUE

Date of completion of the search

5 January 1999

Examiner

Van Humbeeck, F

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 11 7472

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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